

(12) UK Patent Application (19) GB (11) 2 311 075 (13) A

(43) Date of A Publication 17.09.1997

(21) Application No 9708530.2

(22) Date of Filing 26.04.1997

(71) Applicant(s)

Zeneca Limited

(Incorporated in the United Kingdom)

15 Stanhope Gate, LONDON, W1Y 6LN,
United Kingdom

(72) Inventor(s)

Peter Gregory

Ronald Wynford Kenyon

(74) Agent and/or Address for Service

John Mayall

**Zeneca Specialties, PO Box No42, Intellectual
Property Group, Hexagon House, Blackley,
MANCHESTER, M9 8ZS, United Kingdom**

(51) INT CL⁶

C09B 57/00, C09D 11/10

(52) UK CL (Edition O)

C4P PBS PBS4A P104 P106 P122 P126

U1S S1390 S1392 S1565 S1567

(56) Documents Cited

EP 0031698 A1

**Chemical Abstracts, Vol. 85, abstr no 110104 & DE
2460491**

(58) Field of Search

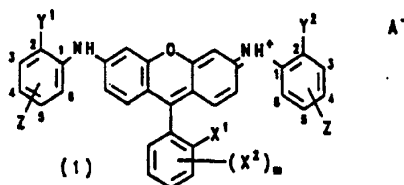
UK CL (Edition O) C4P PBS

INT CL⁶ C09B 57/00

Online: CAS ONLINE

(54) Ester or amide containing xanthene dyes for use in ink jet or hot melt inks

(57) A compound of Formula (1):



wherein:

X^1 is an ester group or an amide group (eg of a carboxylic or sulphonic acid) or a fatty amine salt of a sulphonic acid;

each X^2 independently is a substituent;

m has a value of from 0 to 2;

Y^1 and Y^2 are each independently H, alkyl or halo;

each Z independently is an ester or amide group; and

A^- is an anion.

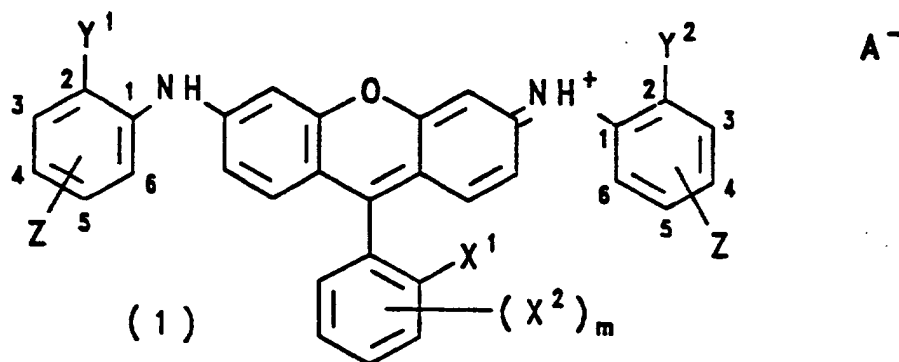
The compound is useful as a colorant for toners, D2T2 printing, plastics, polyesters, nylons and inks, especially inkjet or hot melt inks.

GB 2 311 075 A

CHEMICAL COMPOUNDS

This invention relates to xanthene compounds having ester or amide groups and to processes for their preparation and use. The compounds may be used as coloured toners in photocopiers, in D2T2 printing or as a colorant for plastics, polyesters, nylons or inks, particularly inks used in phase change ink jet printing.

According to the present invention there is provided a compound of Formula (1):



wherein:

X¹ is an ester or amide group or a fatty amine salt of a sulphonic acid;

each X² independently is a substituent;

m has a value of from 0 to 2;

Y¹ and Y² are each independently H, alkyl or halo;

each Z independently is an ester or amide group; and

A⁻ is an anion.

It is preferred that X¹ is an ester or amide group, especially an ester group.

A preferred ester group is of the formula -CO₂R¹ or -SO₂OR¹ wherein R¹ is optionally substituted phenyl or optionally substituted C₁-20-alkyl, especially a phenyl or C₁-4-alkyl group substituted by 0 to 3 groups selected from halo, especially chloro or bromo; alkyl, especially C₁-4-alkyl; and alkoxy, especially C₁-4-alkoxy.

Examples of preferred ester groups include $-\text{CO}_2(\text{CH}_2)_3\text{CH}_3$, $\text{CO}_2(\text{CH}_2)_2\text{CH}_3$, $\text{CO}_2\text{CH}_2\text{CH}_3$, $\text{CO}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$, $\text{CO}_2\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2)_3\text{CH}_3$, $\text{CO}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ and $\text{CO}_2(\text{CH}_2)_5\text{CH}_3$.

A preferred amide group is of the formula $-\text{CO}_2\text{NR}^2\text{R}^3$ or $-\text{SO}_2\text{NR}^2\text{R}^3$ wherein R^2 and R^3 are each independently H or C_{1-20} -alkyl, more preferably C_{2-10} -alkyl. Preferably R^2 is H and R^3 is C_{1-20} -alkyl.

Preferred fatty amine salts of a sulphonic acid are of the formula $-\text{SO}_3^-\text{M}^+$ wherein M^+ is a quaternary amine containing at least 8 carbon atoms. M^+ is preferably of formula $^+\text{NQ}_4$ wherein each Q independently is H or alkyl, provided that M^+ contains at least 8 carbon atoms, preferably from 8 to 18 carbon atoms. It is preferred that three Qs are H and one Q contains from 8 to 18 carbon atoms.

An especially preferred fatty amine salt is derived from tertiary alkyl primary amine, for example as described in US patent 5,084,099 column 4, line 24 to column 5, line 48, which is incorporated herein by reference thereto.

The nature and position of the substituent or substituents defined by $-(\text{X}^2)_m$ is generally selected on the basis of synthetic convenience. It is preferred that each X^2 independently contains less than 7 carbon atoms. As examples of substituents represented by X^2 there may be mentioned halo, especially chloro; an amide group; alkyl, especially C_{1-4} -alkyl; alkoxy, especially C_{1-4} -alkoxy; and an ester group. It is preferred that m has a value of 1, more preferably 0.

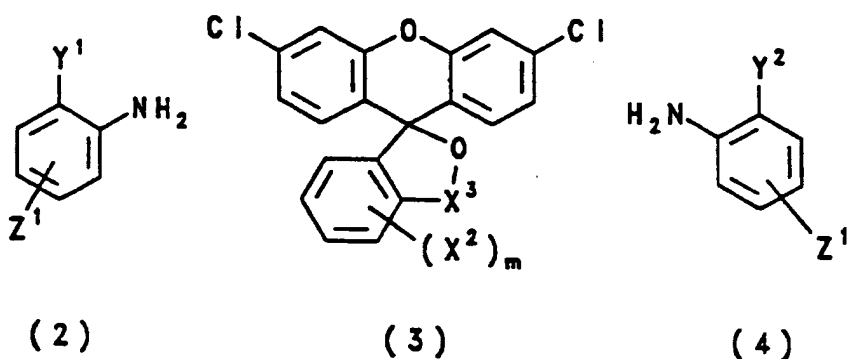
As will be appreciated the compound of Formula (1) can exist in tautomeric forms other than that illustrated and these are intended to be included in the definition provided by Formula (1).

When Y^1 or Y^2 is an alkyl group it preferably has less than seven carbon atoms, and more preferably is C_{1-4} -alkyl, especially methyl. When Y^1 or Y^2 is halo it is preferably chloro. It is preferred that Y^1 and Y^2 are identical to each other.

It is preferred that one or both of the groups represented by Z are at the 5-position indicated in Formula (1). Preferably the groups represented by Z are identical to each other and, in one embodiment, are identical to the group represented by X^1 .

The anion represented by A^- is preferably a colourless anion. Examples of colourless anions include a carbonate, bicarbonate, sulphate, nitrate, bisulphate, acetate, benzoate, halide or phosphate, especially chloride, bromide and sulphate.

The compounds of Formula (1) may be prepared by condensing together compounds of Formula (2), (3) and (4) wherein X^2 , m, Y^1 and Y^2 are as hereinbefore defined, Z^1 is an acid group, preferably a sulpho or carboxy group, and X^3 is $C=O$ or SO_2 , followed by esterification or amidification of the acid groups Z^1 to give a compound of Formula (1):



Condensation of compounds (2), (3) and (4) is preferably performed at a high temperature, more preferably above $150^{\circ}C$, especially in the range $170-190^{\circ}C$. The condensation may be performed in a high boiling solvent, for example sulpholane.

Esterification of the acid groups may be achieved by heating with an alcohol and mineral acid or by converting them to an acid chloride and reacting with an alcohol. It will be apparent to those skilled in the art how acid groups can be converted to an acid chloride, for example carboxy groups may be heated with thionyl chloride and sulpho groups may be heated with chlorosulphonic acid. Methods of converting acid groups to amides (ie, amidification) will also be apparent to those skilled in the art, for example by converting an acid to an acid chloride and reacting an acid chloride with the amine.

Compounds containing both ester and amide groups may be prepared by performing the above described condensation using a compound of formula (2) or (3) where Z^1 is an ester or amide group and subsequently converting any acid group present, for example a carboxy or sulpho group derived from X^3 , to an amide or ester group as desired.

When X^3 is SO_2 a compound of Formula (3) may be condensed in a step-wise manner with a compound of Formula (2) under mild conditions, followed by condensation with a compound of Formula (4) under more forcing conditions. This is of particular value where the compounds of Formula (2) and (4) are different to each other.

The compound of Formula (1) may be used in coloured toners, D2T2 printing, coloured plastics, as a disperse dye for cotton or nylon or as an ink colorant.

The compounds of Formula (1) are especially useful for the preparation of inks, especially phase change inks, used in ink jet printing. The inks can be prepared according to formulations analogous to those known in the art, for example those described in US patents 5,084,099, 4,390,369 or European Patent 0181198. The preferred inks contain up to 10%, or preferably 1-5% (by weight), of a compound of Formula (1) and a vehicle having a melting point in the range 30°C to 130°C. Preferred vehicles having a melting point in the range 30°C to 130°C comprise a paraffin, fatty acid, fatty alcohol or fatty ester or a wax or mixture thereof.

The ink preferably has a maximum viscosity of 50 centipoises, more preferably less than 20 centipoises, especially less than 14 centipoises when molten.

In addition to the above-described components, the ink of the present invention may contain a ketone, preferably having a melting point in the range of 65 to 120°C, for example a stearone or laurone. The ketone preferably does not exceed 50% by weight of said ink. The present inks may optionally also contain up to 4% by weight of a plasticizer, such as an acrylic resin plasticizer, for example as described in European Patent Application 85.305977.2.

The preferred paraffin is a chlorinated paraffin having a chlorine content of 65% to 72% by weight, obtained by chlorinating a paraffin or mixture of paraffins containing from 18 to 35 carbon atoms. Especially preferred paraffins are described in EP 333,335 A2, column 2 lines 17 to 43 which are incorporated herein by reference thereto.

The preferred fatty acid, fatty alcohol or fatty ester vehicle contains from 18 to 26 carbon atoms, especially preferred are C₁₈₋₂₄ alcohols. Stearic acid or behenic acids are suitable fatty acids, behenic presently being preferred over stearic.

The preferred vehicle is a wax, particularly candelilla wax, having a melting point above 65°C. Other waxes believed suitable include bamboo leaf, bees waxes, caranda, carnauba, hydrogenated castor oil, Chinese insect, cotton, cranberry, certain Douglas-fir bark, asparto, certain flax, Indian corn, Madagascar, most micro-crystalline waxes, montan, ouricury, ozocerite, palm, peat wax, rice bran, shellac wax, sisal hemp, sorghum grain, Spanish moss, refined sugar cane waxes and mixtures thereof, each of which waxes has a melting temperature above about 65°C. Mixtures of such waxes found suitable for jetting include 50-50 mixture of candelilla and carnauba wax.

In addition to providing an ink, the present invention also provides a method of ink jet printing comprising the steps of (a) heating an ink as hereinbefore described to a temperature above its melting point, preferably above 80°C, and (b) impulse jetting said ink onto a substrate whereupon said ink solidifies to form a print.

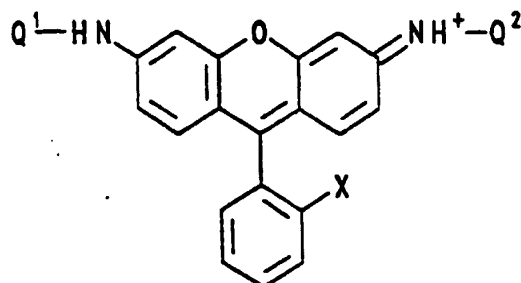
Suitable methods of impulse jetting an ink as hereinbefore described will be apparent to those skilled in the art, for example using a commercially available phase change ink jet printer.

The compound of Formula (1) has an attractive bright magenta shade, high tinctorial strength and excellent water fastness when printed on plain paper or an overhead projector sheet.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise indicated.

Example 1

Preparation of the compound of Formula (5) where X is n-butoxycarbonyl and Q¹ and Q² are both 2-methyl-5-n-butoxycarbonylphenyl



(5)

Stage a) - Condensation

A mixture of 3,6-dichlorofluoran (7.4g), 3-amino-4-methylbenzoic acid (9.1g), zinc chloride (4.2g) and sulpholane (20g) was stirred at 180°C for 3 hours. After cooling, the mixture was added to ice/water (200g) and concentrated hydrochloric acid (10 ml) was added. The resultant precipitate was filtered off and washed with water.

The precipitate was added to water (600ml) and the pH adjusted to 9.0-9.5 by addition of sodium hydroxide solution. The solution was screened and the filtrate acidified to pH 3 with concentrated hydrochloric acid. The carboxy dye in the free acid form was filtered off, washed with a little water to give a solid and then dried.

Stage b) - Esterification

To 10g of the product of stage a) in n-Butanol (300ml) was added concentrated sulphuric acid SG 1.84 (3ml) and the mixture stirred under reflux for 4 hours. After cooling to room temperature the solution was poured onto water (1 litre). The organic layer was separated from the aqueous layer and dried over Magnesium Sulphate. The dry solution was screened and n-butanol evaporated off leaving an oil. The oil was dissolved in toluene (100ml) and screened. The toluene was evaporated off, hexane added and the title product ($\frac{1}{2}\text{SO}_4^{2-}$ salt) precipitated from the oil as a solid. The product was filtered off and dried, and was found to have a lambda max at 545nm in toluene.

Example 2

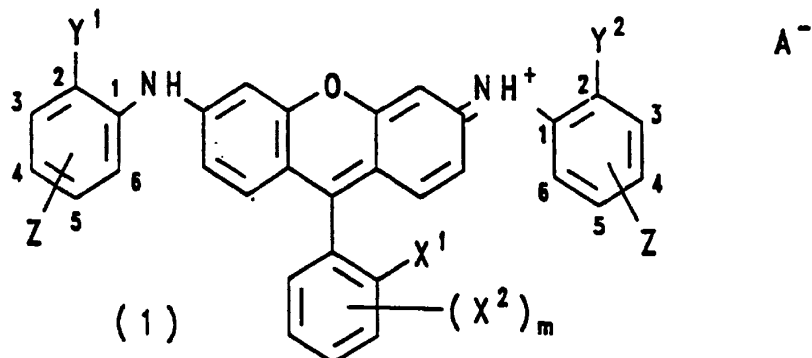
The method of Example 1, Stage a), was repeated and 10g of the product of Stage a) was added to toluene (200ml). One drop of dimethyl formamide was added, followed by dropwise addition of thionyl chloride (8.3g) and the mixture stirred and heated under reflux for 1 hour. Approximately 10ml of the reaction mixture was allowed to distill off to remove excess thionyl chloride. The mixture was cooled to 40°C and 20g of n-butanol added dropwise. The mixture was stirred under reflux for 1 hour and cooled. Further toluene (200ml) was added followed by water (600ml) and the pH adjusted to 9-10 by addition of 2N sodium hydroxide solution.

The resultant organic layer was separated off, washed with water (100ml) and dried over magnesium sulphate. The solvent was then evaporated off and the solid residue dried at 50°C, to give the title product (chloride salt).

A solid phase change ink may be prepared by adding 0.75g of the title dye to a vehicle prepared by mixing Kemamide S-180 (56g, Witco Corporation), Unirez X37-523-235 (a dimer acid based tetra-amide material manufactured by Union Corporation, formed by the reaction of one mole of dimer acid, two moles of ethylenediamine and two moles of stearic acid), Arakawa KE-311 resin (10g) and Naugard 524 (0.1g) at 110°C to give a homogenous solution, and removing any solids by filtration. The ink so prepared may be used to print paper using a conventional phase change ink jet printer.

CLAIMS

1. A compound of Formula (1):



wherein:

- X^1 is an ester or amide group or a fatty amine salt of a sulphonic acid;
 - each X^2 independently is a substituent;
 - m has a value of from 0 to 2;
 - Y^1 and Y^2 are each independently H, alkyl or halo;
 - each Z independently is an ester or amide group; and
 - A^- is an anion.
2. A compound according to Claim 1 wherein X^1 is an ester group.
3. A compound according to Claim 2 wherein X^1 is an ester group of the formula $-CO_2R^1$ or $-SO_2OR^1$ wherein R^1 is optionally substituted phenyl or optionally substituted C_{1-20} -alkyl.
4. A compound according to any one of the preceding claims wherein X^2 contains less than 7 carbon atoms.
5. An ink comprising upto 10% of a compound according to any one of Claims 1 to 4 and a vehicle having a melting point in the range $30^\circ C$ to $130^\circ C$.

6. An ink according to Claim 5 having a viscosity of up to 50 centipoises when molten.
7. A method of ink jet printing comprising the steps of (a) heating an ink according to Claim 5 or 6 above its melting point and (b) impulse jetting the ink onto a substrate whereupon the ink solidifies to form a print.
8. A substrate printed by a method according to Claim 7.
9. Use of a compound defined in Claim 1 as a colorant in a hot melt ink jet printing ink.



Application No: GB 9708530.2
Claims searched: 1-9

Examiner: Stephen Quick
Date of search: 4 August 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C4P (PBS)

Int Cl (Ed.6): C09B 57/00

Other: Online: CAS ONLINE

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	EP 0031698 A1 (POLAROID), see example 1b pages 17 & 18	-
A	Chemical Abstracts, Vol. 85, abstr no 110104 & DE 2460491 (HOECHST), see abstract	-

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

